Indian J. Phys. **49**, 628-630 (1975)

Vibrational assignments of rhenium oxide tetrafluoride from normal coordinate analysis

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(*Received* 27 *December* 1974)

A partial assignment of the vibrational modes of $ReOF_4$ has been reported by Paine *et al.* (1973) from Raman and Infrared spectral measurements. An attempt is made here to assign the fundamentals by normal coordinate analysis using Wilson FG matrix method. The assignment was assisted by the previous work on vibrational analysis of $ReOF_4$ by Deshpande & Joshi (1975) It was possible to obtain a satisfactory assignment as well as a set of potential energy constants.

The possible structures of $ReOF_4$ molecule come under the point groups C_{2v}, C_{3v} and C_{4v}. From the available experimental data Paine *et al* (1973) have favoured the C_{4v} structure. The nine normal modes are classified as $3a_1$, $2b_1+1b_2+3e$. All modes are Raman active while only a_1 and e are infrared active.

Assignments : The four stretching modes are classified as $2a_1+1b_1+1e$. Out of these the modes at 1072 cm^{-1} and 701 cm^{-1} are assigned to the a_1 species, while the one at 722 cm^{-1} is assigned to the e species by Paine *et al* (1973). The only other stretching mode which appears in the Raman spectrum is a weak mode at 667 cm^{-1}. This mode compares with a similar mode of $ReOF_5$, hence is chosen as the b_1 stretching mode.

While the assignment of stretching modes is unambigous there is no straight forward method for assigning the bending modes. The five bending modes fall under $1a_1+1b_1+1b_2+2e$. The reported modes in the low frequency region are 303, 256, 245, 216 and 168 cm^{-1}. The force field calculations are now tried to assign the five bending modes to the different species by the process of repeated trials. These trial sets of assignments were now used to carry out normal coordinate calculations for a general valance force field. The internal coordinates defined are identical with those reported by Stefanson & Jones (1952) for MOX_4 type of molecule (figure 1). The kinetic energy matrix (G) elements are evaluated by the usual S_{kt} vector method.

Structural parameters used in the calculations are reported by Edwards & Jones (1968). The secular equations were solved by method of successive approximations and the force constants along with calculated frequencies are

reported in table 1. Also the most suitable vibrational assumption of the fundamental modes of $ReOF_4$ is given in table 1.

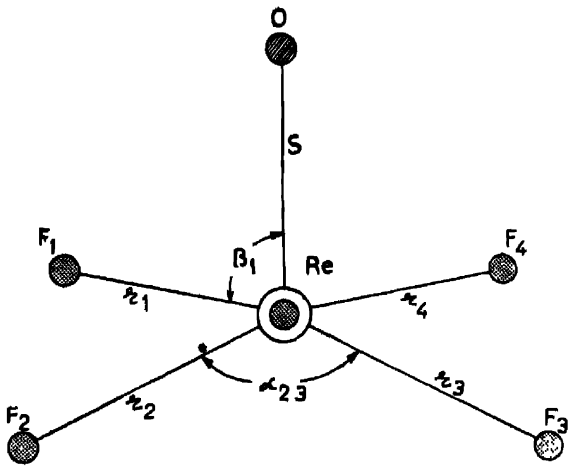

Fig. 1

Table 1—Molecular parameters, force constants and observed and calculated frequencies for $ReOF_4$

Molecular Parameters	Vibrational Frequencies cm^{-1}		Force constants m.dynes/Å
	Observed	Calculated	
		a_1 species	
Re-O = 1.65 Å	1072	1078	f_S = 10.0797
Re-F = 2.3 Å	701	662	f_r = 4.7744
F-Re-O = 100°	303	333	$f_{rr'}$ = 0.1383
F-Re-F = 81°		b_1 species	
	667	667	f_{rr} = −0.1005
	245	245	f_α = 0.1241
		b_2 species	
	256	256	$f_{\alpha\alpha}$ = −0.0302
		e species	
	722	705	f_β = 1.4122
	216	235	$f'_{\beta\beta}$ = 1.3946
	168	158	$f_{\alpha\beta}$ = 0.1063

The stretching force constant between rhenium and oxygen atoms is 10·0797 m.dynes/Å for $ReOF_4$, while it is 8·3575 m.dynes/Å for $ReOF_5$ molecule. This result is in accordance with the fact that as the coordination number of the central atom increases, the force constant decreases.

Acknowledgment

The authors wish to thank Shri V. C. Deshpande and Shri A. C. Risbud for their interest in the present work. One of the authors (R.S.J.) wishes to thank Dr. V. A. Puntambekar, Head of the Physics Department, Fergusson College, Poona-4, for his encouragement.

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